Imenen, afgeleid van methylsulfonylacetonitrile

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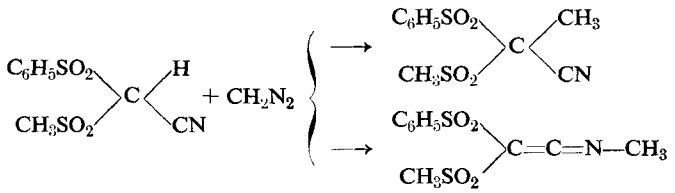
SUMMARY.

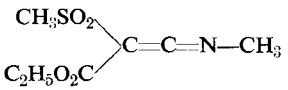
When reacting diazomethane on nitriles of the type RSO_2CHXCN, where X is a negative group, we expected to obtain derivatives of propionitrile. In several cases, however, this reaction yielded compounds methylated on the nitrogen atom, which have been called imenes.

Thus two reactions are possible, e.g.:

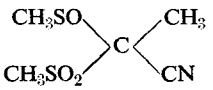


In the case of bis-methylsulphonyl-acetonitrile, the imene is formed exclusively: $(CH_3SO_2)_2C{=}C{=}N{-}CH_3$.

When X represents the carboxethyl group, only the imene could be isolated:



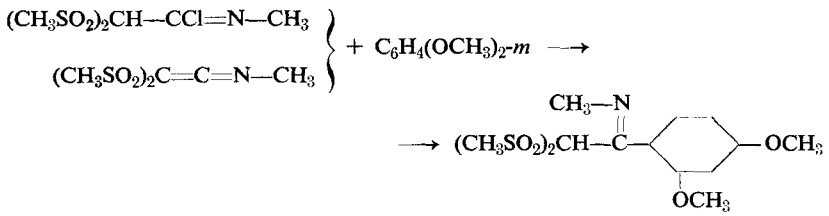
Finally, methylsulphoxyl-methylsulphonyl-acetonitrile, which is less acidic, forms only the C-methyl derivative:



There seems to be a connection between the dissociation constant of the acetonitriles and their ability to react in tautomeric form.

Imenes add amines most readily and react also with other nucleophilic reagents, such as water, alcohols, mercaptans, hydrogen sulphide, hydrocyanic acid.

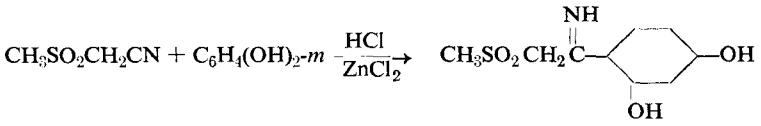
Bis-methylsulphonyl-N-methylimene was studied more extensively and proved to possess not only electrophilic but also nucleophilic properties. Thus it adds HCl and gives the Friedel-Crafts reaction e.g.:



It is believed that the reaction of HCl with bis-methylsulphonyl-N-methylimene begins with an attack by a proton on the nitrogen atom, followed by the addition of a chlorine ion.

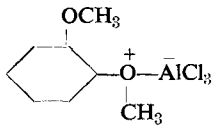
It is remarkable that methylsulphonyl-carboxethyl-N-methylimene does not react at all with resorcinol-dimethylether, which is generally active in the Friedel-Crafts reaction.

The second part of the thesis deals with the Houben-Hoesch reaction given by some alkyl-sulphonyl-acetonitriles e.g.:



It is shown that the influence of the medium is of great importance. In the presence of $AlCl_3$ the H.H. reaction between methylsulphonyl-acetonitrile and benzene occurs readily. Under the same conditions, it was impossible to couple this nitrile with veratrol, though here a higher activity might have been expected.

Undoubtedly, this lack of activity is owing to the formation of an addition compound of the following type which de-activates the benzene nucleus by its -I-effect:



As the activity of acetonitrile is enhanced by the introduction of a methylsulphonyl group, we should expect a still higher activity, when acetonitrile is substituted by two methylsulphonyl groups. However, it proved to be impossible to couple bis-methylsulphonyl-acetonitrile even with the active compound resorcinol.

In alkaline solutions ω-methylsulphonyl-acetophenones bearing

hydroxyl groups on places 2, 4 and 6 of the benzene nucleus show an absorption maximum at 334 mμ, owing to bivalent ions of the type: